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Supporting information

$[Cp^*RhCl_2]_2$: Mechanosynthesis and applications in C–H bond functionalisations under ball-milling conditions

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1. General Information

^1H NMR spectra were recorded at 300 MHz, 400 MHz or 600 MHz in $CDCl_3$. Chemical shifts are reported in delta (δ) units in parts per million (ppm). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded at 150 MHz. Chemical shifts are reported against the central line of the $CDCl_3$ triplet at δ 77.0 ppm for $CDCl_3$. Mass spectra were acquired on a Finnigan SSQ 7000 spectrometer. Elemental analyses were performed on an Elemantar Vario EL instrument. Melting points were measured with a Büchi Melting Point B-540 apparatus.

Mechanochemical reactions in the planetary ball mill were carried out in a FRITSCH Planetary micro mill model "Pulverisette 7 classic line", using 12 mL milling vessels

made of tungsten carbide or zirconium oxide with 20 milling balls (5 mm in diameter) of the same material. Reactions in the mixer mill were conducted in a RETSCH Mixer Mill MM 400, using 10 mL milling jars made of stainless steel with one ball (10 mm in diameter) made of the same material.
The reactions were monitored by thin layer chromatography using plates coated with silica gel 60F254 (Merck), or aluminum oxide ALOX N/UV254 (Macherey-Nagel). Column chromatography purifications were performed using silica gel 60 or neutral Al_2O_3 from Merck. Unless otherwise noted, starting materials were purchased from commercial suppliers and used without further purification.

2. Procedure for the mechanosynthesis of $[Cp^*RhCl_2]_2$ (4)

A mixture of $RhCl_3(H_2O)_n$ (**2**, 0.15 g, 0.576 mmol) and 1,2,3,4,5-pentamethyl-cyclopentadiene (**3**, 0.118 g, 0.868 mmol, 1.5 equiv) was milled under LAG[1] conditions (η = 0.25; MeOH) in a 12 mL tungsten carbide milling vessel with 20 tungsten carbide milling balls (5 mm in diameter) in a planetary mill at 800 rpm for 3h. After the milling was completed, Rh dimer **4** was isolated by column chromatography using SiO_2 and a mixture of DCM:MeOH (v:v = 50:1) as eluent. An alternative isolation protocol consisted in washing the reaction mixture with 10 mL of pentane to eliminate the excess of **3**. Then the crude was dissolved in a minimum volume of chloroform follow by the slow addition of pentane until a dark red solid precipitated from the solution.

3. General procedure for the Rh(III)-catalysed C-H bond halogenation of 2-phenylpyridine in the ball mill

A mixture of 2-phenylpyridine (**5,** 54.3 mg, 0.349 mmol), NXS (2.2 equiv), $AgSbF_6$ (48.07 mg, 0.139 mmol, 0.4 equiv) and $[Cp^*RhCl_2]_2$ (**4**, 10.81 mg, 0.017 mmol, 5.0 mol%) was milled in a 10 mL stainless steel milling jar with 1 stainless steel milling ball (10 mm in diameter) in a mixer mill at 30 Hz for 3 h. After the milling was completed, the products (**6** or **7**) were isolated by column chromatography using SiO_2 and a mixture of pentane:EtOAc (v:v = 15:1) as eluent.

4. Procedure for the mechanosynthesis of the rhodacycle 8

A mixture of $[Cp^*RhCl_2]_2$ (**4**, 75 mg, 0.121 mmol), 2-phenylpyridine (**5**, 41.41 mg, 0.266 mmol) and sodium acetate (60 mg, 0.733 mmol) was milled in a 12 mL ZrO_2 milling vessel with 20 ZrO_2 milling balls (5 mm in diameter) in a planetary mill at 500 rpm for 3 h. After the milling was completed, rhodacycle **8** was isolated by column chromatography using neutral Al_2O_3 and a mixture of DCM:MeOH (v:v 100:1) as eluent.

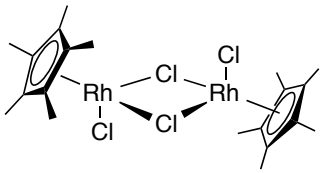
5. Stoichiometric reaction between rhodacycle 8 and NBS

A mixture of **8** (50 mg, 0.117 mmol), NBS (45.8 mg, 0.257 mmol, 2.2 equiv) and $AgSbF_6$ (40.2 mg, 0.117 mmol, 1.0 equiv) was milled in a 10 mL stainless steel

milling jar with 1 stainless steel milling ball (10 mm in diameter) in a mixer mill at 30 Hz for 3 h. After the milling was completed, product **6** was isolated by column chromatography using SiO_2 and a mixture of pentane:EtOAc (v:v = 15:1) as eluent.

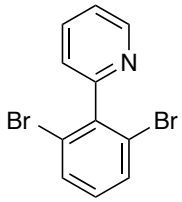
6. Characterisation data for products 4, 6, 7, and 8

Pentamethylcyclopentadienylrhodium(III) chloride dimer (4)



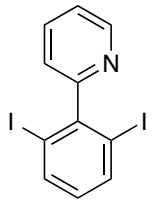
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.62 (s, 30H, C_5Me_5).
^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 94.27 (d, J_{RhC} = 9 Hz, C_5Me_5), 9.55 (s, C_5Me_5).
Dark red solid, melting point: > 350°C (decomposes). IR (KBr): ν = 2975, 2910, 1458, 1371, 1162, 1022, 733cm^{-1}. $C_{20}H_{30}C_{l4}Rh_2$ (618.07): calcd. C 38.87, H 4.89; found C 38.34, H 4.82.
MS (EI): *m*/*z* = 307 (1, M^+/2), 272 (10), 236 (20), 137 (68), 102 (100), 91 (54), 77 (30).
Data is in accordance with the literature.[2]

2-(2,6-dibromophenyl)pyridine (6)



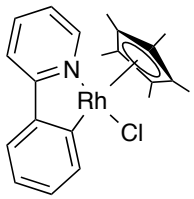
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.74 (ddd, *J* = 4.8, 1.7, 1.0 Hz, 1H), 7.80 (td, *J* = 7.7, 1.7 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.37-7.27 (m, 2H), 7.12 (t, *J* = 8.2 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 158.9, 149.7, 142.0, 136.6, 132.0, 130.7, 124.7, 123.9, 123.1.
Off-white solid, melting point: 72-73°C. IR (KBr): ν = 2924, 2320, 1739, 1568, 1411, 1272, 1179, 1050, 987, 721 cm^{-1}.
MS (EI): *m*/*z* = 314 (6), 312 (9, M+), 310 (4), 234 (100), 232 (91), 153 (71), 126 (29).
Data is in accordance with the literature.[3]

2-(2,6-diiodophenyl)pyridine (7)



^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.75 (ddd, *J* = 4.8, 1.1, 1.0 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.81 (td, *J* = 7.7, 1.8 Hz, 1H), 7.34 (ddd, *J* = 7.7, 5.0, 1.1 Hz, 1H), 7.25 (dt, *J* = 7.8, 1.0 Hz, 1H), 6.74 (t, *J* = 8.0 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 164.4, 149.5, 148.4, 139.2, 136.7, 131.3, 124.2, 123.4, 97.0.
Off-white solid, melting point: 123-125°C. IR (KBr): ν = 2923, 2328, 1748, 1560, 1405, 1265, 1179, 991, 757 cm^{-1}.
MS (EI): *m*/*z* = 407 (5), 406 (32, M+), 280 (100), 153 (95), 126 (45).
Data is in accordance with the literature.[3]

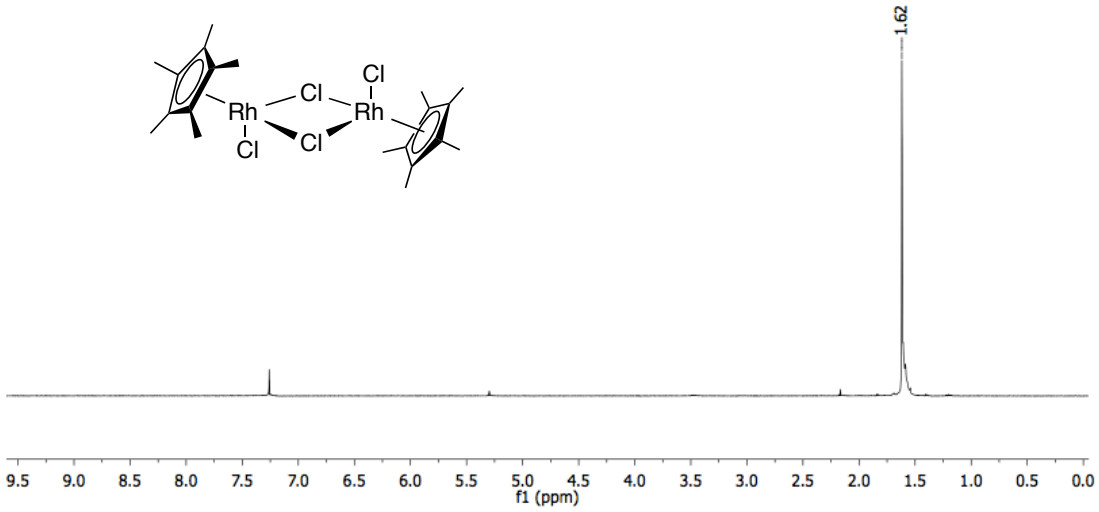
Rhodacycle 8



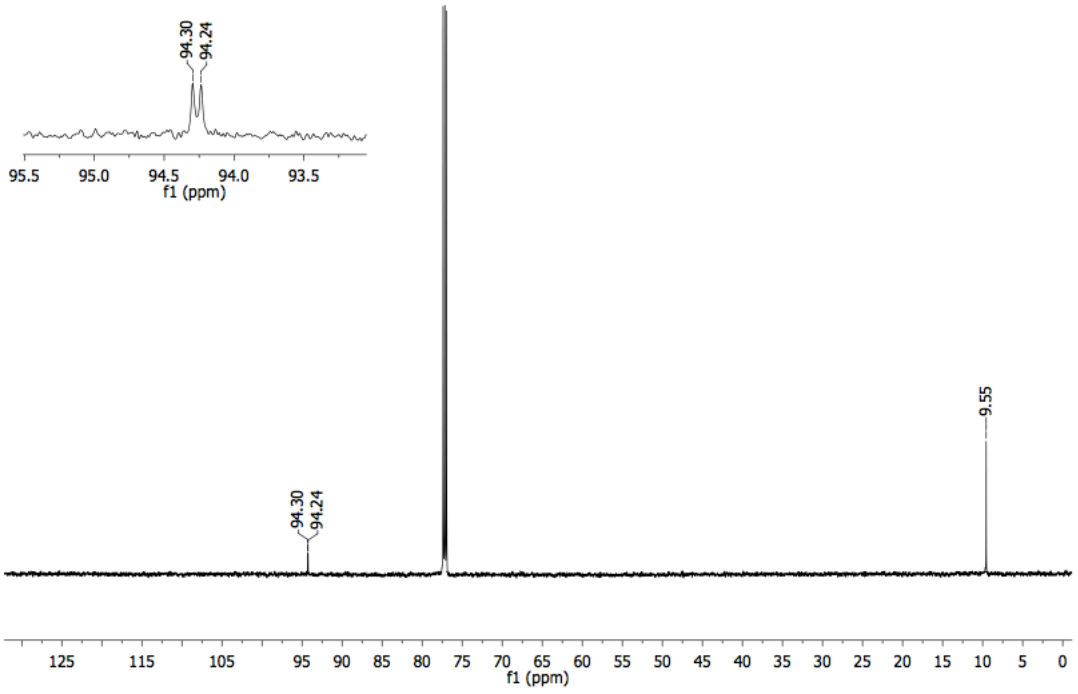
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.73 (d, *J* = 5.4 Hz, 1H), 7.80 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.72-7.67 (m, 1H), 7.59 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.23 (dd, *J* = 7.6, 1.4 Hz 1H), 7.25-7.20 (m, 1H), 7.11 (ddd, *J* = 7.2, 5.6, 1.5 Hz, 1H), 7.07-7.01 (m, 1H), 1.63 (s, 15H).
^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 178.7 (d, $^{1}J_{Rh\text{-}C}$ = 32.1 Hz), 165.5, 151.4, 143.8, 137.1, 136.9, 130.5, 123.5, 122,8, 122.0, 119.1, 96.0 (d, $^{1}J_{Rh\text{-}C}$ = 6.5 Hz, C_5Me_5), 9.2.
Red-orange solid, melting point: > 260°C (decomposes). IR (KBr): ν = 3035, 2913, 1740, 1578, 1456, 1017, 745 cm^{-1} .
MS (EI): *m*/*z* = 426.9 (1, M+), 256 (6), 234 (33), 189 (100), 119 (39).
Data is in accordance with the literature.[4]

7. ^{1}H and ^{13}C NMR Spectra.

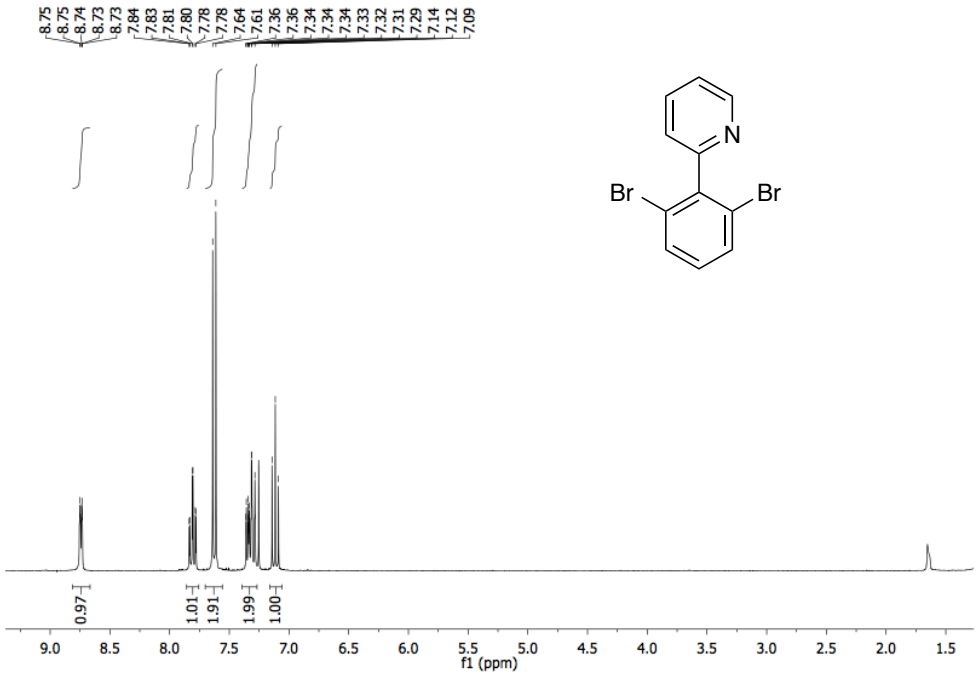
^{1}H NMR spectrum of $[Cp^*RhCl_2]_2$ (4)



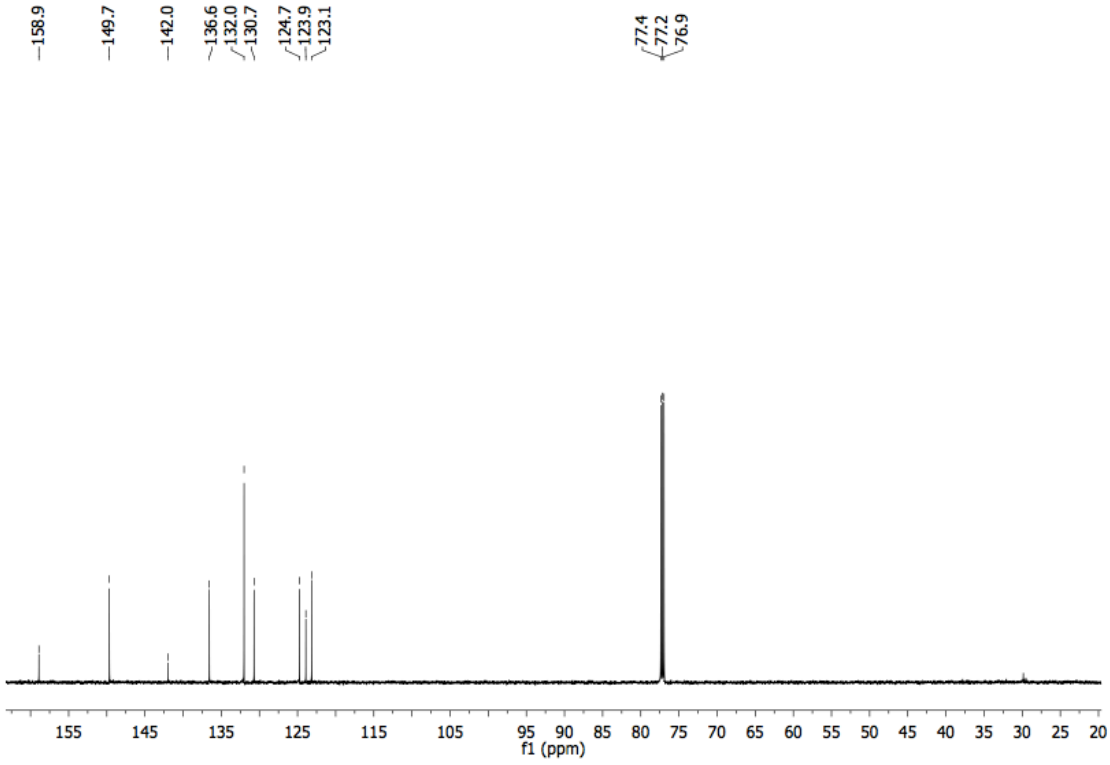
^{13}C NMR spectrum of $[Cp^*RhCl_2]_2$ (4)



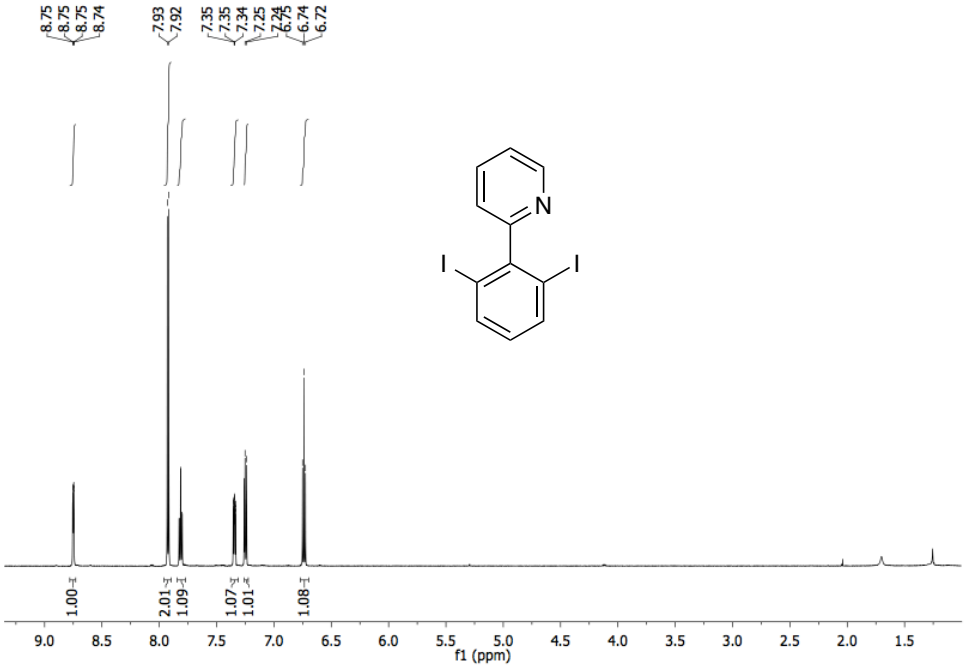
^{1}H NMR spectrum of 2-(2,6-dibromophenyl)pyridine (6)



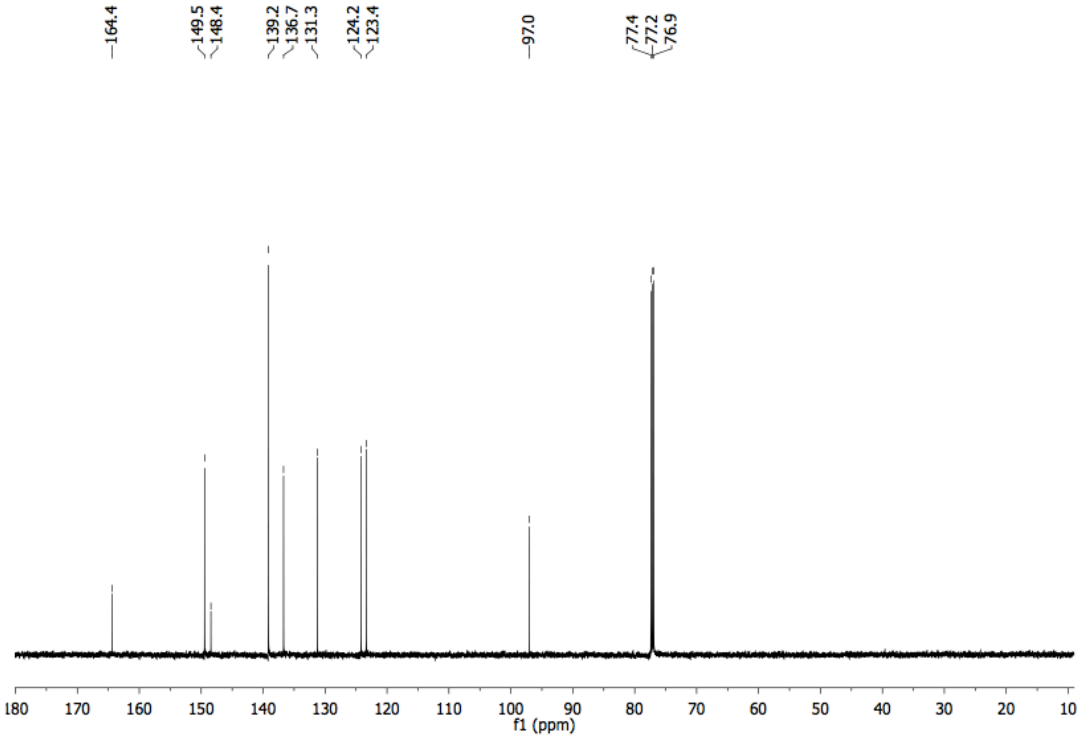
^{13}C NMR spectrum of 2-(2,6-dibromophenyl)pyridine (6)



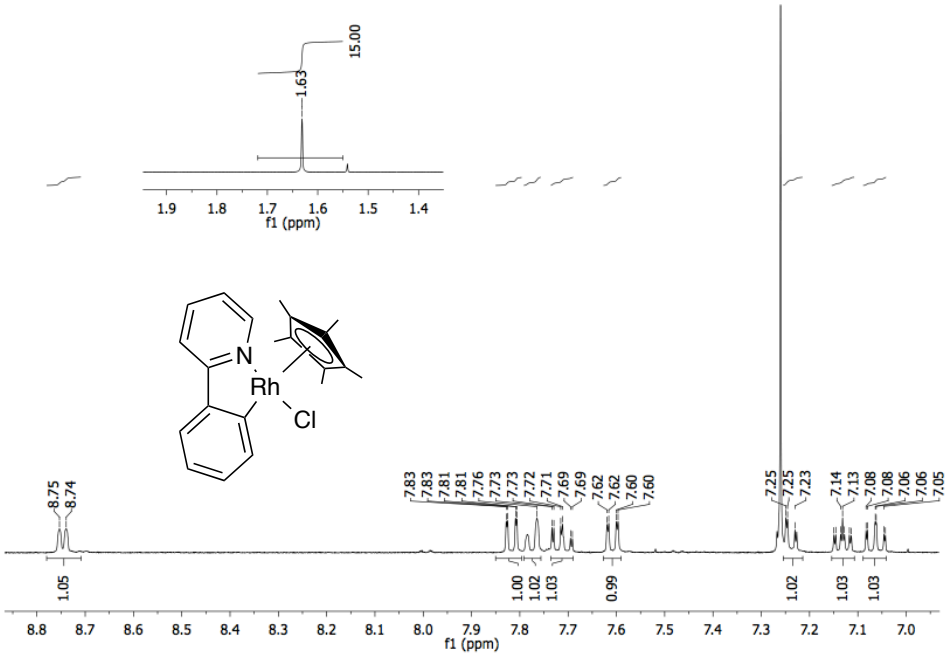
^{1}H NMR spectrum of 2-(2,6-diiodophenyl)pyridine (7)



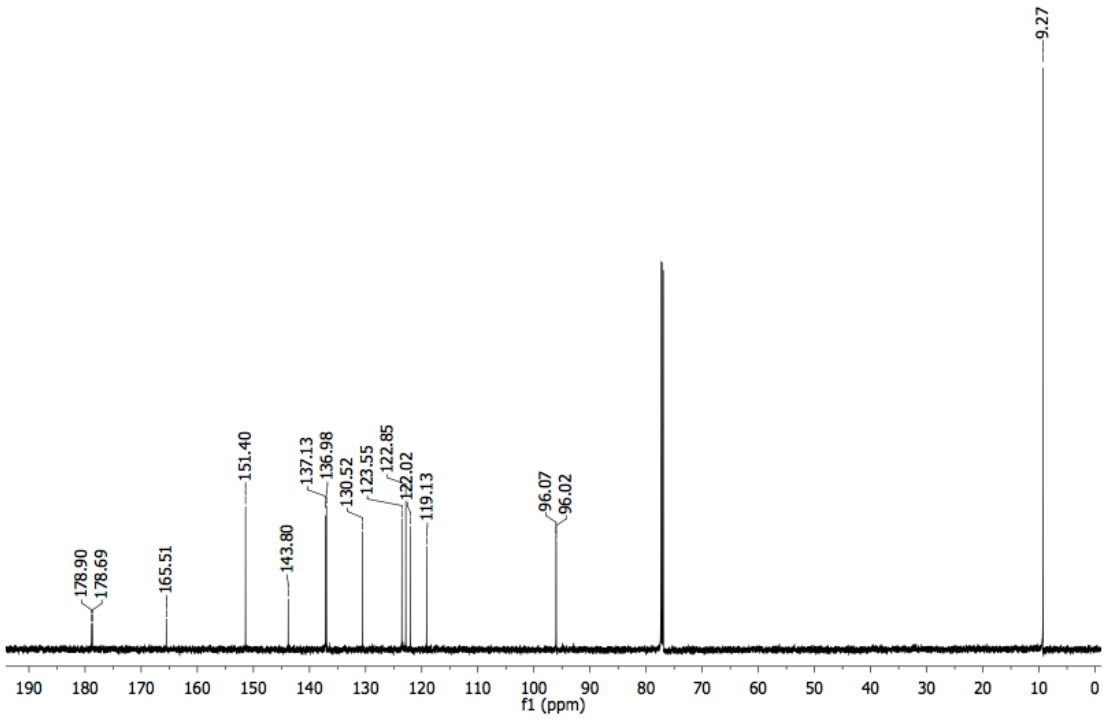
^{13}C NMR spectrum of 2-(2,6-diiodophenyl)pyridine (7)



^{1}H NMR spectrum of rhodacycle 8



^{13}C NMR spectrum of rhodacycle 8



8. Figure 1. ^{1}H NMR analysis of the mechanochemical synthesis of $[Cp^*RhCl_2]_2$ (4)

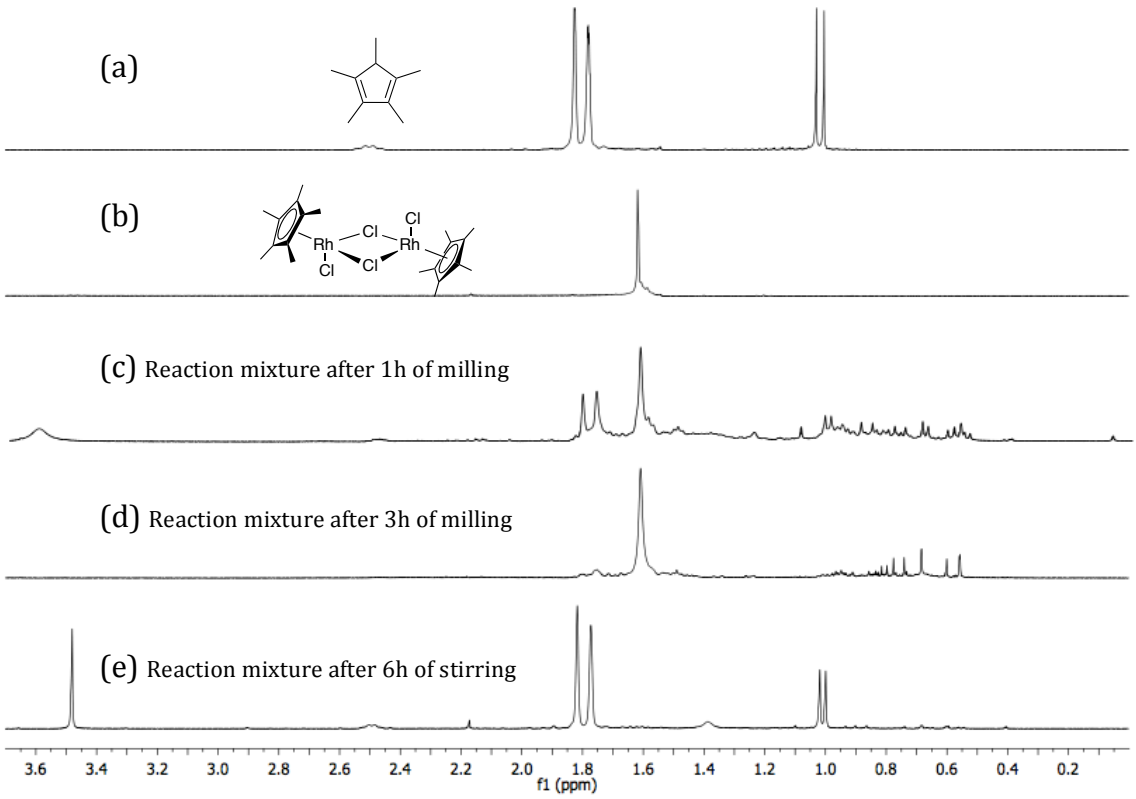


Figure 1. ^{1}H NMR spectra in $CDCl_3$ of: (a) Cp*H (**3**); (b) mechanochemically prepared $[Cp^*RhCl_2]_2$ (**4**); (c) reaction mixture of $RhCl_3$ hydrate (**2**, 0.576 mmol) and Cp*H (**3**, 2.0 equiv) after 1 h of LAG[1] (η = 0.25; MeOH); (d) reaction mixture of $RhCl_3$ hydrate (**2,** 0.576 mmol) and Cp*H (**3**, 2.0 equiv) after 3 h of LAG[1] (η = 0.25; MeOH) (e) reaction mixture of $RhCl_3$ hydrate (**2,** 0.058 mmol), Cp*H (**3**, 2.0 equiv) and methanol (8.2 μL) in $CDCl_3$ (0.8 mL) after 6 h of stirring at room temperature.

9. References

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